



# Materials

## Lower-Conductivity Thermal-Barrier Coatings

**Additional stabilizers are incorporated into yttria-stabilized zirconia.**

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Thermal-barrier coatings (TBCs) that have both initial and post-exposure thermal conductivities lower than those of yttria-stabilized zirconia TBCs have been developed. TBCs are thin ceramic layers, generally applied by plasma spraying or physical vapor deposition, that are used to insulate air-cooled metallic components from hot gases in gas turbine and other heat engines. Heretofore, yttria-stabilized zirconia (nominally comprising 95.4 atomic percent  $\text{ZrO}_2$  + 4.6 atomic percent  $\text{Y}_2\text{O}_3$ ) has been the TBC material of choice. The lower-thermal-conductivity TBCs are modified versions of yttria-stabilized zirconia, the modifications consisting primarily in the addition of other oxides that impart microstructural and defect properties that favor lower thermal conductivity.

TBCs are characterized by porosity, typically between 5 and 20 percent. Porosity reduces the thermal conductivity of a TBC below the intrinsic conductivity of a fully dense (that is, non-porous) layer of the TBC material. The thermal conductivity of a TBC increases as its porosity is reduced by the sintering that occurs during use at high temperature. For future engines that will operate at higher gas temperatures, TBCs with greater degrees of both initial insulating

capability and retention of insulating capability will be needed.

The present lower-thermal-conductivity TBCs are made of  $\text{Zr}_2\text{O}_2$  and  $\text{Y}_2\text{O}_3$  doped with additional oxides that are chosen to perform three functions:

- Create thermodynamically stable, highly defective lattice structures with tailored ranges of defect-cluster sizes to exploit the effectiveness of such structures as means of attenuating and scattering phonons, thus reducing thermal conductivity;
- Produce of highly distorted lattice structures with essentially immobile defect clusters and/or nanoscale ordered phases, which effectively reduces concentrations of mobile defects and movements of atoms, thus increasing sintering-creep resistance; and
- Exploit the formation of complex nanoscale clusters of defects to increase the measures of such desired mechanical properties such as fracture toughness.

The additional oxides in a TBC according to this concept are typically selected as a pair — one from each of two groups of oxides denoted for this purpose as groups A and B. Group A includes scandia ( $\text{Sc}_2\text{O}_3$ ) and ytterbia ( $\text{Yb}_2\text{O}_3$ ). These oxides are highly stable, and the radii of their trivalent cations are smaller than

those of the primary dopant yttria. Group B includes neodymia ( $\text{Nd}_2\text{O}_3$ ), samaria ( $\text{Sm}_2\text{O}_3$ ), and gadolinia ( $\text{Gd}_2\text{O}_3$ ) which are also highly stable, and their trivalent cations are larger than those of yttria.

Like yttria, the A and B oxides are regarded as stabilizers. Preferably, the total stabilizer content (yttria + A oxide + B oxide) should lie between 4 and 50 atomic percent. The concentration of yttria should exceed that of each of other stabilizers, and the concentrations of the A and B oxides should be approximately equal. Formulations other than the foregoing preferred one are also possible: Variations include the use of alternative group-A oxides (e.g.,  $\text{MgO}$ ,  $\text{NiO}$ ,  $\text{Cr}_2\text{O}_3$ ), the use of two or more group-A and/or group-B oxides, substitution of hafnia for zirconia, and substitution of other primary stabilizers (e.g., dysprosia or erbia) for yttria.

*This work was done by Robert A. Miller of Glenn Research Center and Dongming Zhu of Ohio Aerospace Institute. Further information is contained in a TSP (see page 1).*

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## Process for Smoothing an Si Substrate After Etching of $\text{SiO}_2$

**Reactive-ion etching can be tailored to minimize undesired side effects.**

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A reactive-ion etching (RIE) process for smoothing a silicon substrate has been devised. The process is especially useful for smoothing those silicon areas that have been exposed by etching a pattern of holes in a layer of silicon dioxide that covers the substrate. Applications in which one could utilize smooth silicon surfaces like those produced by this process include fabrication of optical waveguides, epitaxial deposition of silicon on selected areas of silicon substrates, and prepara-

tion of silicon substrates for deposition of adherent metal layers.

During etching away of a layer of  $\text{SiO}_2$  that covers an Si substrate, a polymer becomes deposited on the substrate, and the substrate surface becomes rough (roughness height  $\approx 50$  nm) as a result of over-etching or of deposition of the polymer. While it is possible to smooth a silicon substrate by wet chemical etching, the undesired consequences of wet chemical etching can include compro-

mising the integrity of the  $\text{SiO}_2$  sidewalls and undercutting of the adjacent areas of the silicon dioxide that are meant to be left intact.

The present RIE process results in anisotropic etching that removes the polymer and reduces height of roughness of the silicon substrate to  $<10$  nm while leaving the  $\text{SiO}_2$  sidewalls intact and vertical. Control over substrate versus sidewall etching (in particular, preferential etching of the substrate) is